

EFFECTS OF THERMAL HYDROCRACKING ON THE
COMPOUND-TYPE DISTRIBUTION IN ATHABASCA BITUMEN

A.E. George, R.C. Banerjee, G.T. Smiley and H. Sawatzky

INTRODUCTION

Upgrading Athabasca bitumen requires the use of pyrolytic processes. The currently-used coking processes are wasteful, and alternatives such as the thermal hydrocracking process are sought (1). This report deals with the hydrocarbon-type conversions involved in hydrocracking this asphaltic sulphurous bitumen.

Five samples of hydrocracked bitumen, selected to represent increasing severities of treatment as expressed in pitch conversion to distillable fractions, were subjected to analysis by liquid-solid chromatography.

EXPERIMENTAL

A schematic diagram of the procedure and the breakdown to compound types is shown in Figure 1.

Thermal Hydrocracking

The hydrocracking pilot plant and its operation have been described in a previous report (1). The reactor is a vertical vessel to which the total Athabasca bitumen and hydrogen are fed at the bottom. Any gases formed can escape upwards immediately and are removed in a scrubber before the hydrogen is recycled with the fresh make-up hydrogen to the reaction vessel. Five samples representing increasing degrees of hydrocracking were selected for investigation. Three of these samples are representative of steady state conditions of a liquid hourly space velocity of 2, a feed rate of 8000 grams per hour and temperatures of 435, 445 and 455°C respectively. Similarly, the other two samples were obtained at a liquid hourly space velocity of 1, a feed rate of 4000 grams per hour and temperatures of 445 and 460°C respectively. All the samples resulted from processing at 2000 psi operating pressure and a hydrogen recycle rate of 1.5 cu ft/hr at operating pressure and 25°C. The hydrogen purity was 85%. The product was separated into a light and a heavy oil in a hot receiver vessel.

Distillation

The light oil was separated by distillation (ASTM D216-54) to light ends boiling below 200°C and the fraction boiling above 200°C. The heavy oil

did not contain any light ends boiling below 200°C. The distillation residue above 524°C is defined as pitch.

Deasphalting

The asphaltene portion of the heavy oil was precipitated through the addition of twenty volumes of pentane to one volume of oil. The asphaltenes were separated by filtration, extracted with pentane in a soxhlet extractor and dried first on a water bath, then under reduced pressure at 50°C. The main pentane solubles and washings were combined and n-pentane was completely evaporated from these maltenes.

Compound-Type Separation

The light ends distilling below 200°C were analyzed for saturate, aromatic and olefinic contents on silica gel using the fluorescent indicator adsorption method (ASTM D1319-70).

The light oil fraction boiling above 200°C and the deasphalted heavy oil (maltenes) were separated into compound-type concentrates of saturates, monoaromatics, diaromatics, polyaromatics, polar material and basic compounds in a dual-packed (silica gel and alumina gel) liquid-solid chromatographic column developed by the API project 60 (2), and modified in our laboratory (3). The modification consisted of scaling down the original procedure by a factor of 10 and applying pressure to increase the speed of separation. The polyaromatics were eluted by benzene; the polar material was eluted by a mixture of polar solvents (methyl alcohol, ethyl ether and benzene) and the basic compounds were eluted by pyridine at 100°C (Figure 1).

The number of moles of the various types of structures were determined using average molecular weights that were obtained by vapour pressure osmometry for the light oil and heavy oil. The average molecular weights of the light oil fraction below 200°C were determined from gas chromatographic simulated distillation data, assuming that the material distilling when half of the sample had distilled represented the average molecular weight. The aromatics in the light ends distilling below 200°C were assumed to be mononuclear aromatics.

The number of sulphur-bearing structures in each fraction was determined assuming that there was one sulphur atom per molecule. The number of sulphur-free structures was then obtained by difference.

Mass Spectrometric Analyses

Analyses of the approximate compositions of the cyclic saturates were performed on a C.E.C. 21-104 mass spectrometer, operated at an ionization potential of 70eV and using electric scan.

RESULTS

The Athabasca bitumen is a heavy, sulphurous oil with high asphaltene and metal contents. The chemical nature of its hydrocarbons is mostly aromatic, 75% by wt, with a prevalent polyaromatic-polar composition of 70% of the aromatics. The properties of the bitumen are given in Table 1.

Effect of Thermal Hydrocracking on the Gross Composition

Increasing hydrocracking severity causes a steady increase in the amounts of light oil (Table 2) at the expense of the heavy oil and asphaltene contents. The asphaltene content diminishes from 15.3% in the feedstock and 13.4% at 435°C (LHSV-2) to 2.7% at 460°C (LHSV-1). This is an appreciable decrease, considering that the molecular weights of the treated asphaltenes also decline. In these cracking reactions, asphaltenes could be formed as well as destroyed. The presence of hydrogen pressure would suppress asphaltene formation. The percentage of heavy oil in the product decreases steadily to 54% of its content when the severity of the operating temperature was increased from 435°C (LHSV-2) to 460°C (LHSV-1). This effect is even more pronounced considering the lower molecular weight of the products.

The severity of hydrocracking is more pronounced at the lower liquid hourly space velocity due to the increased residence time of the liquids in the reactor. A comparison of the pitch conversions of the two experiments at 445°C and space velocities of 1 and 2 is given in Table 2.

Effect of Thermal Hydrocracking on the Compound-Type Distribution

The compound-type distribution on a weight basis is shown in Table 3. The sulphur is included with the aromatic and polar types. Tables 4 and 5 show the number of moles per 100g of bitumen for the hydrocarbons and for the sulphur compounds respectively.

Saturated Hydrocarbons:

The total percentage of saturates in the liquid products of the bitumen increases markedly with increasing severity of hydrocracking, particularly in the light ends. Although the saturate content remains almost constant in the light oil fraction above 200°C, the increasing percentage of this fraction in the total product increases the total saturate content.

An approximate mass spectrometric ring analysis of the saturates of the Athabasca bitumen shows that they are mainly cyclic with little or no alicyclics. About 90% of the cyclic material is dicyclic, tricyclic and tetracyclic in equal proportions. Monocyclics are absent, and pentacyclics or higher ring systems are present in only small amounts. The alicyclic hydrocarbons developed because of hydrocracking. The dicyclic and tricyclic systems prevailed, followed by the monocyclics, then the tetracyclics, or the reverse, depending on the investigated boiling range. Pentacyclic molecules decreased to trace amounts, while 6- and higher- ring structures disappeared.

The saturate content includes olefinic hydrocarbons ranging in the light oil below 200°C from 8.0% to 5.2% in the least and most severely hydrocracked products respectively. It ranges from 14.6% to 3.0% in the light oil products above 200°C.

Mononuclear Aromatics:

The monoaromatic content of the bitumen increases drastically (175%) at the highest pitch conversion rate and about half of this increase takes place at the mildest treatment (Table 3). The number of aromatic rings, however, increases 3.7 times (Table 4), mostly in the form of benzene structures in the light oil. Benzene compounds are valuable as chemical feedstocks and because of their combustion characteristics.

The numbers of sulphur structures in the monoaromatic concentrate, mostly thiophenes, double on the mildest treatment and then remain almost constant (Table 5).

Dinuclear Aromatics:

This fraction's weight per cent decreases slightly on hydrocracking (Table 3) but the number of its diaromatic rings doubles (Table 4). The thermal stability of the associated sulphur structures are indicated by their slight decrease (Table 5) with no evidence of formation from the destruction

of higher molecular weight components. We have evidence (6) that most of these sulphur compounds are alkyl benzothiophenes.

Polynuclear Aromatics:

The weight per cent of this fraction decreases by more than 50% on hydrocracking, and 54% of this decrease occurs at the least severe treatment (Table 3). However, the number of the polyaromatic structures increases 2.75 times in the mildest treatment, then gradually to 5 times at 460°C (Table 4). The associated sulphur components are unstable relative to the diaromatic sulphur structures (Table 5) and they decrease by 30% with the mildest treatment. This percentage increases gradually to 65% at 460°C.

Polar Components:

Although this fraction diminishes in weight with hydrocracking similar to the polynuclear aromatics (Table 3), the number of these polar structures increase (Table 4). The joining sulphur structures are thermally unstable and decrease to 40% at 460°C (Table 5).

Basic Compounds:

More than half of these compounds are destroyed at the mildest temperature, and only 15% remain at 460°C.

DISCUSSION

The increase of the saturated hydrocarbons content is caused by the cleavage of aliphatic components from the aromatic, polar and asphaltenic structures. At the mildest treatment this fraction appears to increase mostly at the expense of the polynuclear aromatics and the polar materials. The other types would also lose paraffinic and cyclic portions to the saturate fraction and in the meantime receive the same from the higher molecular weight complex fractions. The saturated hydrocarbons could, to a large extent, represent cleavage products from the asphaltenes, especially in the last two treatments. There is a strong relationship between the rate of asphaltene destruction and the increase in saturates content (Tables 1, 2 and Figure 2).

There is also a relationship between the mole increase of the sulphur-free monoaromatic structures (benzenes) and the degree of asphaltenes

conversion (Figure 2) which suggests that these benzenes are cleaved from the complex asphaltenic structures. However, they could be generated by the aromatization of cycloalkanes.

Asphaltenes are considered to consist mainly of large substituted polynuclear aromatic structures (4) and to contain more heteroatoms than the other bitumen fractions. Therefore, it would be expected that their cleavage during cracking should increase the polynuclear aromatic structures as well as the polar compounds. While there is a steady increase in these fractions (Table 4), there is no direct relationship between this increase and the rate of asphaltene destruction.

The only compound types that increase in sufficient quantity to explain the diminishing asphaltene content in the two most severe treatments are the saturates and the mononuclear aromatics. Since it is not plausible to assume that the asphaltenes consist largely of benzene structures, a hydrogenation step of the asphaltene clusters before undergoing cracking must be considered to explain the increase in monoaromatics.

It is unlikely that hydrogenation consumes appreciable molecular hydrogen and the major consumption is probably due to reaction with free radicals formed on cracking, unless some inorganic components in the bitumen catalyze hydrogenation. Probably the hydrogenation of most of the polynuclear aromatic clusters in the asphaltenes and some of the polynuclear aromatic fractions occur by hydrogen transfer reactions. Tetralins are good hydrogen donors in these reactions but, if this is the case, then there would be an appreciable increase in the dinuclear aromatic structures of the products where asphaltenes decrease sharply. This was not observed.

It is known that cyclohexanes are not good hydrogen donors but decalins are (5). If the addition of one aliphatic ring to cyclohexane would increase its hydrogen-donating capability greatly, then it can be inferred that the addition of more saturated rings would result in even better donors. The saturated hydrocarbons are highly cyclized and thus should be effective hydrogen donors. For these reasons, it can be argued that the large complex aromatic clusters become hydrogenated during the hydrocracking reactions by hydrogen resulting from aromatization of saturated structures and that the hydrogenated structures undergo more extensive cracking. This explains the large increase in both the benzene structures and saturated hydrocarbons.

ACKNOWLEDGEMENT

The authors are grateful to the Process Engineering Section for the provision of samples and the processing data.

LITERATURE

- (1) Merrill, W.H., Logie, R.B. and Denis, J.M., Mines Branch Report R-281 (1973)
- (2) Hirsch, D.E., Hopkins, R.L., Coleman, H.J., Cotton, F.O. and Thompson, C.J., ACS Preprints, Div. of Petrol. Chem., p. A65 (1972)
- (3) Sawatzky, H., George, A.E., Smiley, G.T. and Montgomery, D.S., Fuel, 55, 16 (1976)
- (4) Yen, T.F., Energy Sources, 1, 447 (1974)
- (5) Carlson, C.S., Langer, A.W., Stewart, J. and Hill, R.M., Industrial and Engineering Chemistry, 50, No. 7, 1067 (1958)
- (6) Clugston, D.M., George, A.E., Montgomery, D.S., Smiley, G.T. and Sawatzky, H., ACS Fuel Division preprints, 19, No. 2, 202 (1974)

TABLE 1

PROPERTIES OF ATHABASCA BITUMEN

Specific Gravity, 60/60°F	1.009
Sulphur, wt%	4.63
Ash, wt%	0.68
Viscosity, cSt at 210°F	152.2
Conradson Carbon Residue, wt%	12.8
Asphaltene (pentane insolubles), wt%	15.3
Benzene Insolubles, wt%	0.9
Nickel, ppm	70.
Vanadium, ppm	190.

TABLE 2

GROSS COMPOSITION OF ATHABASCA BITUMEN AND

HYDROCRACKING PRODUCTS

(wt % of total bitumen)

SAMPLE	PITCH CONVERSION* wt %	GAS*	LIGHT OIL		HEAVY OIL	
			Below 200°C	Above 200°C	MALTENES	ASPHALTENES
FEED			1.4	(83.3% maltenes above 200°C)	15.3	
LHSV-2, 435°C	59.1	3.9	7.0	10.2	65.5	13.4
LHSV-2, 445°C	68.9	4.0	11.5	10.2	62.0	12.3
LHSV-2, 455°C	77.4	5.9	13.1	10.8	59.7	10.5
LHSV-1, 445°C	80.0	6.8	13.5	25.7	47.0	7.0
LHSV-1, 460°C	91.4	9.2	18.5	34.0	35.6	2.7

(*) Reference 1

TABLE 3

DISTRIBUTION OF THE TOTAL COMPOUND-TYPES
IN THE FEED AND HYDROCRACKED
PRODUCTS OF ATHABASCA BITUMEN
 (Wt % of total bitumen)

<u>SAMPLE</u>	<u>SATURATES</u>	<u>MONOAROMATICS</u>	<u>DIAROMATICS</u>	<u>PNA*</u>	<u>PM*</u>	<u>BC*</u>
Feed	21.0	9.6	9.3	20.1	19.0	5.7
LHSV-2, 435°C	31.3	13.1	8.2	14.2	12.8	2.3
LHSV-2, 445°C	32.8	15.0	8.4	12.9	11.6	2.1
LHSV-2, 455°C	36.0	14.7	8.7	11.7	9.8	1.6
LHSV-1, 445°C	39.0	15.0	7.7	11.1	10.5	1.2
LHSV-1, 460°C	44.1	16.8	7.2	9.1	8.8	0.9

* PNA = Polynuclear aromatics
 PM = Polar material
 BC = Basic compounds

TABLE 4

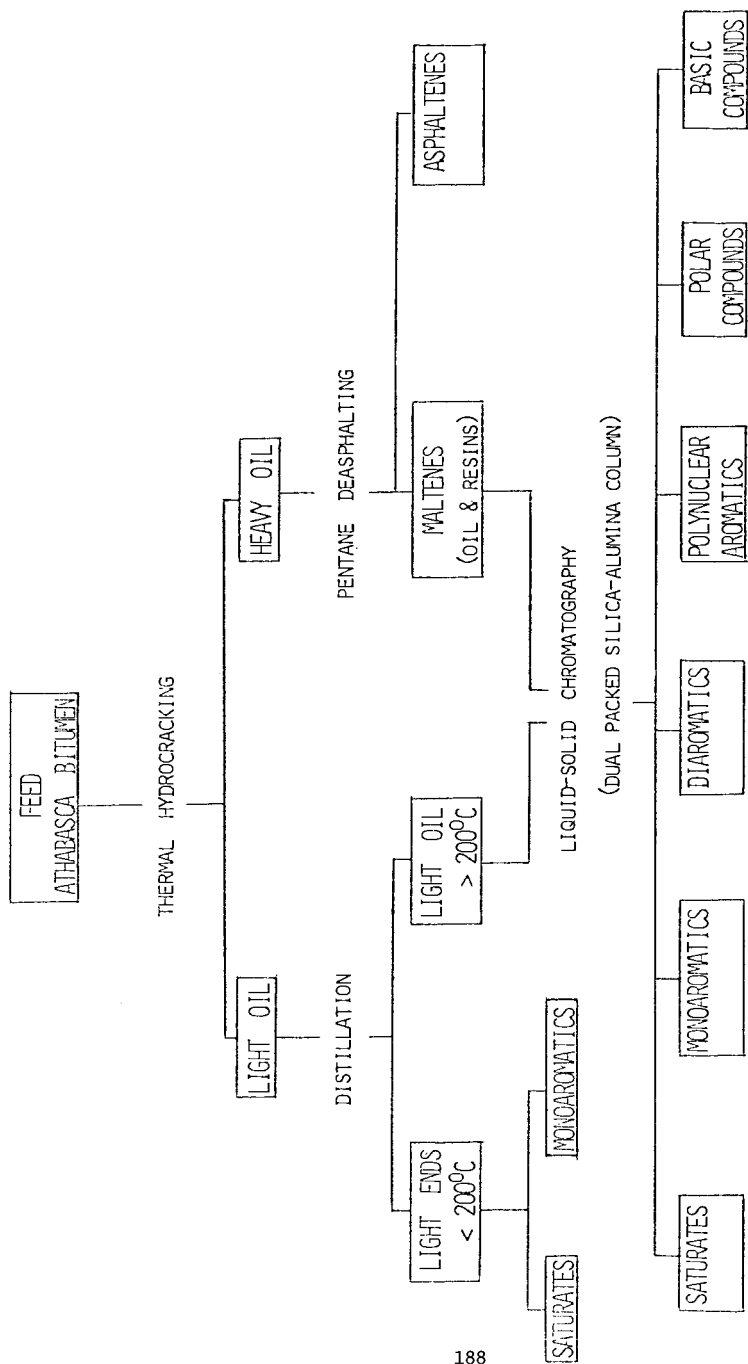
MOLES OF STRUCTURE TYPES
PER 100 GRAMS BITUMEN (SULPHUR COMPOUNDS NOT INCLUDED)

<u>SAMPLE</u>	<u>MONOAROMATICS</u>	<u>DIAROMATICS</u>	<u>POLYAROMATICS</u>	<u>POLAR MATERIAL</u>
FEED	0.021	0.010	0.004	-
LHSV-2, 435°C	0.043	0.015	0.011	0.005
LHSV-2, 445°C	0.058	0.015	0.014	0.008
LHSV-2, 455°C	0.059	0.019	0.015	0.010
LHSV-1, 445°C	0.065	0.020	0.021	0.010
LHSV-1, 460°C	0.078	0.021	0.020	0.013

TABLE 5

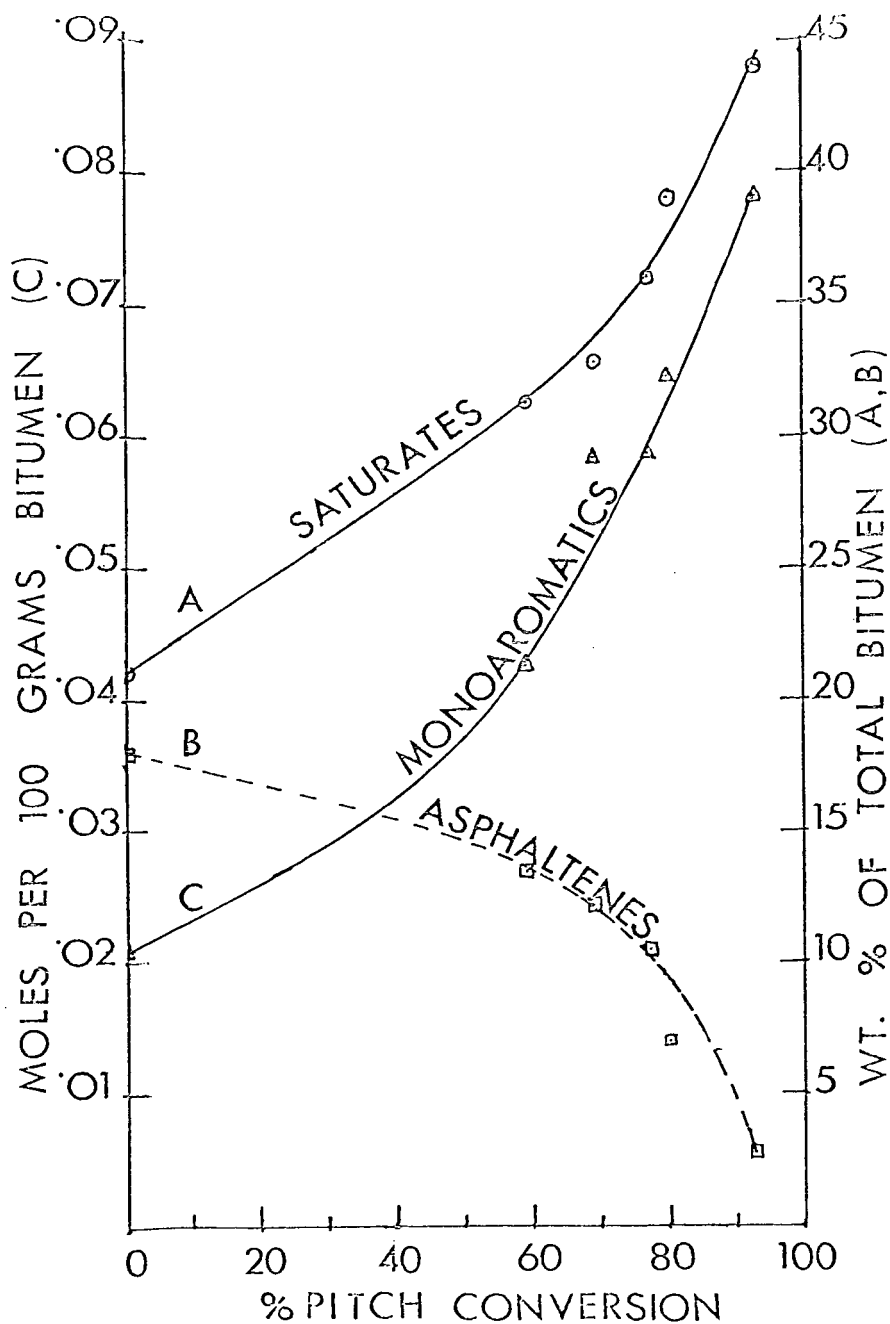
MOLES OF SULPHUR STRUCTURE TYPES
PER 100 GRAMS BITUMEN

<u>SAMPLE</u>	<u>MONOAROMATICS</u>	<u>DIAROMATICS</u>	<u>POLYAROMATICS</u>	<u>POLAR MATERIAL</u>
FEED	0.006	0.014	0.043	0.040
LHSV-2, 435°C	0.012	0.013	0.030	0.025
LHSV-2, 445°C	0.013	0.013	0.026	0.022
LHSV-2, 455°C	0.012	0.013	0.024	0.018
LHSV-1, 445°C	0.011	0.010	0.019	0.018
LHSV-1, 460°C	0.011	0.010	0.015	0.016



HYDROCRACKING AND SEPARATION SCHEMATIC

FIGURE 1



THE EFFECT OF HYDROCRACKING ON SATURATE, MONOAROMATIC AND ASPHALTENE CONTENTS IN ATHABASCA BITUMEN

FIGURE 2